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UNIVERSITY OF PENNSYLVANIA

I. A Separation of Arsenic, Antimony and Vanadium from Tungsten

II. On the Complex Bismuthico tungstates

A THESIS PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

ORLAND RUSSELL SWEENEY

EASTON, PA.:
ESCHENBACH PRINTING COMPANY
1916

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ACKNOWLEDGMENT.

The author wishes to express his sincere thanks to Dr. Edgar F. Smith under whose direction and personal encouragement this study was undertaken.

I. A SEPARATION OF ARSENIC, ANTIMONY AND VANADIUM FROM TUNGSTEN.

INTRODUCTION.

A great number of separations of various elements have been effected, in this laboratory, by passing various gases, or vapors, over the heated samples.[1]

Smith and Oberholtzer[2] found that tungsten was not volatile in hydrogen chloride, and because of this fact it was thought that a separation of this metal from some of those elements which are volatile in hydrogen chloride might be satisfactorily effected.

In his study of the complex inorganic acids Gibbs[3] pointed out that there were no good methods for the analysis of those bodies containing tungsten and the various other elements which he introduced. The investigators cited above found that many of those elements were volatile in hydrogen chloride.

With these thoughts in mind a study of the separation of arsenic, antimony and vanadium from tungsten was begun; and methods have been developed which, it is believed, will satisfactorily effect their separation and estimation.

PREPARATION OF MATERIAL.

All reagents used in this work were carefully purified.

Nitric acid was prepared by mixing a good grade of the commercial product with sodium hydrogen phosphate

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[1] Smith and Hibbs: Jour. Amer. Chem. Soc., **16**, 578. Smith and Hibbs: Zeit. f. anorg. Chem., **7**, 41. Smith and Oberholtzer: Jour. Amer. Chem. Soc., **15**, 1. Smith and Maas: Zeit. f. anorg. Chem., **5**, 280; Jour. Amer. Chem. Soc., **17**, 682. Smith and Meyer: Jour. Amer. Chem. Soc., **17**, 735. Moyer: Jour. Amer. Chem. Soc., **18**, 1029. Keeley and Smith: Jour. Amer. Chem. Soc., **18**, 1096. Smith and Field: Jour. Amer. Chem. Soc., **18**, 1051 and others.

[2] Zeit. f. anorg. Chem., **4**, 236.

[3] Amer. Chem. Jour., **2**, 281.

and distilling. The middle portions were collected separately and again distilled.

Hydrochloric acid was prepared pure by treating the "C. P." acid with copper wire to remove traces of arsenic, after which the hydrogen chloride was expelled from its water solution with sulphuric acid; the gas was collected in pure redistilled water.

Tungsten trioxide was prepared from crude sodium tungstate by the method of Smith and Exner.[1] After recrystallizing the crude tungstate twice the trioxide was precipitated with nitric acid, and was boiled in the mother liquor until it settled well. It was then washed by decantation until it began to settle slowly, after which it was covered with water and ammonia was distilled into it until nearly everything had dissolved. The solution, after decanting from the excess of trioxide, was evaporated on the water-bath and allowed to crystallize. The crystals of ammonium tungstate were added to hot nitric acid, and treated with hydrochloric acid as recommended by the investigators cited above. The trioxide obtained in this manner was again dissolved in ammonia, and the same procedure repeated three times. The resulting trioxide had a uniform yellow color, and portions of it left no residue when treated with two per cent sodium carbonate solutions.[1]

Sodium carbonate was purified by treating the "C. P." product with a few grams of calcium carbonate and fusing in a platinum dish. The melt was dissolved in water, filtered, and carbon dioxide passed in until the sodium acid carbonate separated. The acid carbonate was drained, centrifuged and ignited to the normal carbonate. This was dissolved and again precipitated.

Sodium tungstate was prepared by mixing the purified trioxide with a little more than the theoretical amount of sodium carbonate, fusing in platinum, and recrys-

[1] Proc. Amer. Phil. Soc., 43, 176.

tallizing the product twice. Since sodium carbonate cannot be completely removed from sodium tungstate by recrystallization,[1] the tungsten content was determined by analysis. Potassium tungstate was prepared in a similar manner.

Sodium pyroarsenate was prepared by recrystallizing a good grade of sodium hydrogen arsenate, gently igniting to expel the water of crystallization, and finally igniting, at 200° C. for an hour. The heating should be very gentle at first or the arsenate melts, and dissolves in its own water of crystallization.

Potassium arseno-tungstate was prepared by the Method of Gibbs.[2] Solutions of the 5 : 12 potassium tungstate and potassium di-hydrogen arsenate were mixed, and after evaporating on the water-bath, a white soluble body separated. It was filtered, washed and dried on the water-bath.

Potassium antimonio-tungstate was prepared by boiling a solution of potassium tungstate with an excess of potassium hydrogen pyro-antimonate for about four hours. The suspended matter was then filtered out and on standing a white crystalline precipitate separated. It was filtered, washed with cold water, and dried over calcium chloride.

Vanadio-tungstic acid was prepared by dissolving pure sodium tungstate and sodium vanadate in water and treating with an excess of nitric acid. The reddish brown precipitate which resulted was washed and dried on the water-bath.

SEPARATION OF ARSENIC FROM TUNGSTEN.

The plan adopted was to first subject weighed portions of the arsenate and tungstate, to the action of hydrogen chloride, in order to learn whether, or not, they could be separated quantitatively. Next the arseno-tungstate

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[1] Taylor: U. of P. thesis, 1901.

[2] Amer. Chem. Jour., **2**, 290.

was treated in order to learn whether, or not, a separation could be effected when they were combined chemically.

The apparatus used is shown in Fig. 1. Hydrogen chloride, generated by dropping sulphuric acid into hydrochloric acid, was passed through two wash-bottles containing sulphuric acid. It entered the combustion tube at A, passed over the sample contained in the tube B,

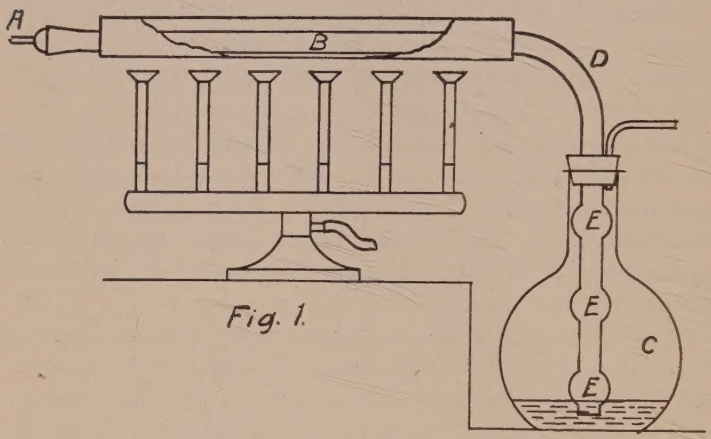

Fig. 1.

and was absorbed in the flask C. The tube was bent at a right angle at D, and contained the bulbs E, E, E, which prevented the liquid in the flask from being drawn back into the tube. The tube rested in an iron trough and was heated by wing-top burners. Glass joints were used throughout, although they were not absolutely necessary.

In order to test the apparatus some pure sodium pyroarsenate was treated with the dry hydrogen chloride. Almost theoretical results were obtained for the residual sodium chloride, and the arsenic was found to be all expelled. The volatilized arsenic was collected in water containing nitric acid. The resulting solution, after boiling to oxidize the arsenic, was made ammoniacal, and the arsenic precipitated with magnesia mixture. The results were invariably low. Careful experiments proved that no arsenic escaped absorption. Various modifications were

made in the procedure, but the method was finally abandoned. Others who have studied this method found it very unsatisfactory.[1]

The procedure which was found most satisfactory for the estimation of the arsenic was as follows: The volatilized arsenic was absorbed in about eight hundred cc. of water. After rinsing out the combustion tube the solution, in the receiver, was diluted to fourteen hundred cc. and was then saturated with sulphur dioxide. After standing one hour the solution was boiled, while a stream of carbon dioxide was passed, until all the sulphur dioxide was removed. Hydrogen sulphide was then passed in until precipitation was complete. The excess of hydrogen sulphide was then removed by a stream of carbon dioxide, the arsenic sulphide filtered on an alundum cone, washed with alcohol, ether, again with alcohol, then carbon disulphide, then with alcohol and finally with ether. After drying to constant weight, at 100° C., it was weighed as arsenic trisulphide. By following this method it was not difficult to get satisfactory results.

Separation and Estimation of Arsenic and Tungsten.—Hibbs[2] attempted to separate tungsten and arsenic mixtures in the form of their sodium salts, but since the sodium tungstate broke up, in part, into sodium chloride and oxides of tungsten he could not calculate the amount of arsenic volatilized from the weight of residual sodium chloride. He succeeded in separating arsenic from pure tungsten trioxide, however, and calculated the amount of arsenic volatilized by subtracting the known amount of trioxide from the residual chloride. Since the amount of tungsten in a sample will not, in general, be known, and since the tungsten will nearly always occur in some combination other than the trioxide, this method, of course, has little practical application. Furthermore,

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[1] Zeit. f. anal. Chem., **1905**, 493.

[2] Jour. Amer. Chem. Soc., **17**, 682.

there is always more or less reduction to the blue oxides when the trioxide is treated with hydrogen chloride.

Weighed portions of the arsenate and tungstate were exposed in a boat, to a stream of hot hydrogen chloride. The tungstate was immediately attached, giving variously colored products, depending upon the temperature. It was found, however, that the arsenic, in the presence of the tungstate, was completely expelled only with great difficulty. It is remarkable that arsenic, when combined with sodium and oxygen ($Na_4As_2O_7$), should be so easily expelled; and when *only mixed* with a tungstate should be so difficult to remove.

A large number of experiments were made to determine the temperature at which a complete separation could be effected. It was found that at too low a temperature the arsenic could not be completely expelled: if the temperature was increased to 300° C. the tungsten began to volatilize. The results of these experiments showed that the temperature at which it was practical to remove the arsenic was dangerously near the point at which the tungsten began to volatilize.

Since only a small amount of the tungsten volatilized at 300° C. (measured by a thermometer lying beside the combustion tube), it was thought best to collect the tungsten which volatilized, rather than to try to regulate the temperature in such a manner as to completely prevent it.

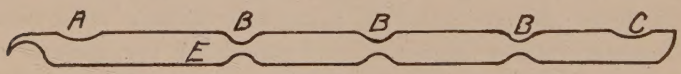

Fig. 2

A tube, about fourteen inches long, which could be pushed into the combustion tube, was constructed as shown in Fig. 2. A was the opening through which the sample was introduced; B, B, B were constrictions, C was the exit.

Procedure: The sample was placed in the tube at E, the tube was then placed in the combustion tube, and

a current of hydrogen chloride was passed over it. The temperature at E was about 300° C., but at the rear end of the tube it was kept much lower to condense any tungsten which might have volatilized. The substance which volatilized was proved to be tungsten, and not an impurity.

By working in this manner it was found possible to completely separate the arsenic and tungsten in about four hours.

After about four hours the receiver was removed, the combustion tube rinsed out, and a second receiver put in place. After another treatment there should be no evidence of arsenic in the second receiver.

The inner tube was removed, its contents rinsed into an evaporating dish with dilute ammonia, and evaporated to dryness on the water-bath. It was then digested on the water-bath with 1 : 1 nitric acid and small quantities of hydrochloric acid were added from time to time. When all action had ceased the watch-glass cover was rinsed off, and the liquid was evaporated. The residue was moistened with nitric acid and evaporated several times to remove all chlorine. The residue, consisting of tungsten trioxide and sodium nitrate, was dissolved in sodium hydroxide, diluted and filtered. A few drops of methyl-orange were added, and the solution was just neutralized with nitric acid. It was then boiled, cooled, and the tungsten precipitated with mercurous nitrate. After standing four hours it was filtered, washed with two per cent mercurous nitrate, and ignited and weighed as tungsten trioxide.

The method of evaporating with nitric acid, and then filtering out the tungsten trioxide, always gave low results. The procedure described—which is really an adaptation of Smith and Exner's method of getting pure tungsten trioxide—gave splendid results.

The following results were obtained:

	Calculated.	Obtained.	Error.
As_2S_3	0.0786	0.0783	—0.0003
WO_3	0.0816	0.0817	+0.0001
As_2S_3	0.0804	0.0808	+0.0004
WO_3	0.0900	0.0898	—0.0002
As_2S_3	0.1470	0.1472	+0.0002
WO_3	0.0796	0.0794	—0.0002

The arsenic was completely expelled from the following mixtures as proved by Marsh's test:

$Na_4As_2O_7$	0.0549	0.1082	0.2010	0.1032
Na_2WO_4	0.1297	0.1084	0.1492	0.1248

It was hoped that the procedure described above would effect a separation of arsenic and tungsten when they were chemically combined. Such was not the case, however. In order to remove the last trace of arsenic, from an arseno-tungstate, it was necessary to pass the hydrogen chloride for six or seven days. This rendered the method useless for practical work.

It was found that moistening the sample a few times with water exposed fresh portions of the unattached salt to the gas, and made it possible to completely remove the arsenic at a much lower temperature, and in a much shorter time. With a tube, such as described above, there was no difficulty attached to this operation. Since there is no danger of loss by spattering, the water could be evaporated in a few minutes.

The modified procedure was as follows: A weighed portion of the arseno-tungstate was brushed into the small tube, and was distributed by rolling and tapping. It was then placed in the combustion-tube and exposed to a stream of hydrogen chloride for about an hour. The temperature, as measured by a thermometer lying beside the combustion tube, should register about 200° C. Since, however, the temperature within the tube varies somewhat with the construction of the apparatus, the proper temperature to use was ascertained by turning the flames gradually higher until the tungsten just began to volatilize, and

condense on the tube, over the sample; a few degrees lower than this was the proper temperature to use. After determining this point the wing-top burners were left permanently adjusted, the gas being regulated at the gas-cock.

After about an hour the apparatus was cooled, the inner tube removed, the sample moistened with water, the tube replaced, and the gas passed for one-half hour longer. This operation was repeated three times.

The receiver was then removed, and the combustion-tube rinsed into it. A second receiver was then put in place, the sample again moistened and the operation repeated. Should the contents of the second receiver show the presence of arsenic, when treated with hydrogen sulphide, it must be added to the first, and the sample must be further treated. The arsenic and tungsten were determined as described above.

The analysis is best made on small samples.

The following results were obtained:

Sample of arseno-tungstate.	Percentage As_2O_5.	Percentage WO_3.
0.1028 g.	11.63	71.01
0.1550	11.57	70.83
0.2858	11.77	70.88
0.2090	...	71.10
0.1409	11.93	70.76
0.2788	11.93	70.91

The method gives satisfactory results, and does not require a longer time than many other analytical procedures which have been generally adopted.

SEPARATION OF ANTIMONY AND TUNGSTEN.

Procedure: Weighed portions of potassium antimonio-tungstate were introduced into the tube, and subjected to the action of hydrogen chloride exactly as described in the separation of arsenic and tungsten. It was found advisable to pass the hydrogen chloride, in the cold, for about one-half hour before lighting the burners.

The alternate treatment with hydrogen chloride and water should be continued until a film of antimony oxychloride no longer forms in the cool portion of the combustion tube. The deposit of oxychloride could be driven into the receiver by "brushing" the combustion tube with the flame of a Bunsen burner.

When the antimony oxychloride no longer condensed in the cool portions of the tube the apparatus was rinsed, the receiver changed, and another put in place. The sample was moistened with water, the water evaporated, and again treated with hydrogen chloride. The second receiver should show, at most, only a slight yellow tinge with hydrogen sulphide.

The tungsten was determined as described under arsenic.

The antimony was precipitated with hydrogen sulphide, filtered through an alundum crucible, ignited in a current of carbon dioxide to constant weight,[1] and weighed as antimony trisulphide.[2]

The methods employed by Gibbs for the analysis of these complexes were described by him as very unsatisfactory. The results obtained varied several per cent, and for that reason it was not possible to check the hydrogen chloride method by another analytical method. Careful tests were made to prove that the antimony was all out of the residue; and care was used to prevent any loss during the process. The following concordant results proved the accuracy of the method:

Samples.	Percentage Sb_2O_5.	Percentage WO_3.
0.1462	66.87	16.07
0.0799	66.84	16.02
0.1090	66.81	15.96
0.1811	...	15.90
0.1582	66.85	15.86
0.3040	67.01	16.05

[1] Treadwell and Hall: Text-book, p. 187.

[2] The carbon dioxide must be free from hydrogen chloride.

SEPARATION OF VANADIUM AND TUNGSTEN.

On passing hydrogen chloride over vanadio-tungstic acid the vanadium came off as a heavy red vapor which condensed to a reddish brown liquid. The residue was soon reduced, however, to a brownish mass which was no longer attacked. By introducing chlorine along with the hydrogen chloride the vanadium was more completely expelled.[1]

Attempts were made to separate the tungsten and vanadium, in a tube, as in the case of arsenic and antimony. After moistening, however, the sample crept so much that the results were always low for tungsten. A distilling bulb was substituted and worked somewhat better. The vanadium condensed in the neck of the bulb, however, and was sometimes drawn into the ground glass joint. For this reason the piece was discarded. After experimenting with several devices the piece shown in Fig. 3 was found to be very satisfactory.

The tube was made in one piece as shown. It consisted of one-inch soft glass tubing A, to which was sealed a one-half inch exit tube, B. To the exit tube a calcium chloride tube was sealed; this prevented the water from being drawn back into the hot tube. The receiver was a large test-tube. The piece was surrounded by a tin box, C, to act as an oven. It was provided with a thermometer. By sealing on D, a small separatory funnel, the sample could be moistened without "breaking" the ground-glass joint E. The dimensions should be about as given. Such a piece is easily cleaned, and the vanadium will not diffuse back to the joint. After it is once started it requires no attention.

Chlorine was generated by dropping hydrochloric acid upon potassium permanganate. Hydrogen chloride was generated in the usual manner. The mixed gases were passed through two wash bottles containing sulphuric acid.

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[1] McAdam: Jour. Amer. Chem. Soc., **32**.

Procedure: Weighed portions of the vanadio-tungstate were introduced into the tube by means of a piece of glazed paper. On passing hydrogen chloride, containing a small amount of chlorine, the sample was attached with the formation of a reddish brown volatile liquid. After a time a

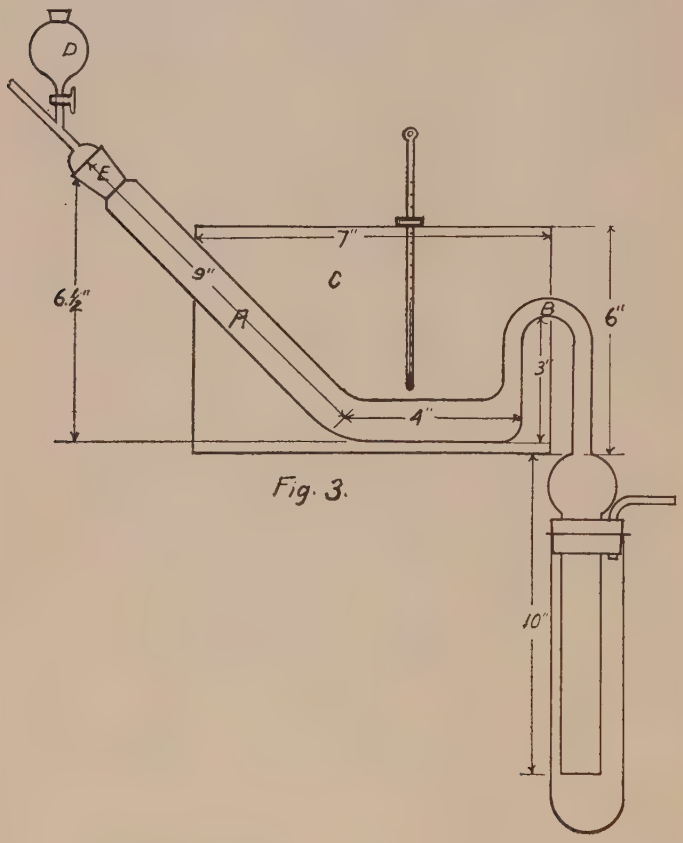

Fig. 3.

gentle heat was applied to the oven, and the temperature was gradually increased until it reached 200° C.

Since too much heat converts this body into a green, non-volatile solid, care should be taken not to heat it too strongly. This green residue is soluble in water, and on

evaporation it again becomes volatile in hydrogen chloride. When the vanadium condenses in the neck of the tube it should be allowed to distill off slowly in the stream of hot hydrogen chloride. The gas was passed rapidly enough to prevent the vanadium from diffusing back to the ground joint.

The receiver contained about one hundred and twenty-five cc. of water, and the exit tube dipped under the water only a short distance.

After about an hour the piece was cooled, and five cc. of 10% sodium hydroxide were added.[1] After evaporating in a stream of the gases it was again heated, for one-half hour, at 200° C. After this it was alternately moistened with water and treated with the gas mixture until the red vanadium compound no longer appeared in the cool portion of the exit tube. The rear end of the tube was then rinsed out, a second receiver put in place, and the operation repeated.

The appearance of this red film proved to be a very delicate test for vanadium. When it no longer appeared the vanadium was always found to be completely expelled. The precaution of an extra treatment was usually observed, however.

The tungsten was removed from the tube with ammonium hydroxide, and was then determined as described under arsenic.

Various methods for determining vanadium were studied, and it was finally decided that the volumetric method using potassium permanganate, was best suited to the conditions presented by the hydrogen chloride method. Experiments were made to prove that there was no loss on evaporating a strong hydrochloric acid solution of vanadium. Such a solution was evaporated, in a retort,

[1] This was necessary since the vanadio-tungstic acid contained no sodium or potassium, and, for that reason, a soluble residue resulted on treating with hydrogen chloride.

the distillate was collected, and failed to show the faintest color with hydrogen peroxide.

The procedure was as follows: The receiver contents, and exit-tube, were rinsed into an evaporating dish, five cc. of concentrated sulphuric acid were added, and the solution evaporated, as far as possible, on the water-bath. It was then heated, over a low flame, until white fumes of sulphuric acid came off. The contents of the dish were next rinsed into an Erlenmeyer flask, diluted to two hundred cc., heated to boiling, and a stream of sulphur dioxide passed in to completely reduce the vanadium to the vanadyl salt.[1] The boiling was continued and a stream of carbon dioxide was passed to remove the excess of sulphur dioxide. When all the sulphur dioxide was expelled the solution was titrated, while still hot, with potassium permanganate. The permanganate was standardized, with pure vanadium pentoxide, which had been reduced in the same manner.

The following results were obtained:

Vanadio-tungstic acid.	Percentage V_2O_5.	Percentage WO_3.
0.2204	...	65.47
0.3396	...	65.31
0.3227	16.17	...
0.3022	15.92	65.35
0.3127	15.90	...
0.2460	15.95	65.20
0.2487	15.95	65.38
0.1848	16.09	65.39

This latter method is so satisfactory that it is recommended in preference to the others. The temperature is easily regulated; the piece can be cooled quickly by removing the oven; the danger of loss from creeping is slight; and the volatile constituent is more quickly removed.

[1] Repeated evaporation with hydrochloric acid will also effect this reduction.

CONCLUSIONS.

1. Methods are given for the separation of arsenic, antimony and vanadium from tungsten, which, it is believed, are more satisfactory than those previously described.

2. Procedures are described which are suitable for estimating the separated constituents.

3. A piece of apparatus has been devised which simplifies the analytical procedures.

II. ON THE COMPLEX BISMUTHICO-TUNGSTATES

In a contribution by Balke and Smith[1] the ammonium, potassium and strontium salts of a bismuthico-tungstic acid, having the composition $3M_2'O.2Bi_2O_3.11WO_3.xH_2O$ were described. In this paper the corresponding mercurous salt is described, and some further observations are recorded.

The ammonium bismuthico-tungstate was prepared by adding small portions of bismuth hydroxide, as it dissolved, to a boiling solution of ammonium para-tungstate. After boiling for two days it was filtered, evaporated to dryness, and extracted with boiling water. On cooling an oil separated from the solution having all the properties of the ammonium bismuthico-tungstate described in the paper cited above. It is worthy of note that this substance had a distinct oily, organic odor when warm. The ammonium salt was dissolved in water and on adding a concentrated solution of potassium bromide the less soluble potassium salt separated.

A solution of the potassium salt was treated with a solution of mercurous nitrate. A light yellow precipitate separated, and, after standing several hours, with occasional shaking, it was filtered and dried. The dry pre-

[1] Jour. Amer. Chem. Soc., **25**, 12.

cipitate was a yellow insoluble powder. On gently igniting it the color deepened to a rich brown; but on stronger heating it began to decompose becoming lemon yellow in color.

Analysis: The mercury was determined by covering the salt with water and adding dilute hydrochloric acid in slight excess. After standing over night it was warmed on the water-bath, filtered into a Gooch crucible, washed with two per cent hydrochloric acid, dried at 100° C. and was then weighed. The residue always contained slight amounts of the undecomposed bismuthico-tungstate. To correct for this the mercurous chloride was expelled by heating the crucible, and the weight of the residue was subtracted from the weight first obtained. The weight of this residue was probably low due to the volatilization of some of the bismuth. (See below.)

The tungsten and bismuth were determined together by gently igniting the mercury salt in a porcelain crucible. The mercury and water were volatilized leaving the oxides of bismuth and tungsten. It is best to place the crucible in a larger crucible, and heat the outer crucible with the flame of a Bunsen burner. If the temperature be too high some of the bismuth will volatilize, and there may be reduction to the blue oxides of tungsten. Better results were obtained by igniting in a weighed amount of sodium tungstate as recommended by Gibbs. The bismuth and tungsten can be separated in the residue by boiling with aqua regia. The crucible contents were covered with aqua regia and evaporated to dryness on the water-bath; it was then treated with 1 : 1 nitric acid, evaporated, again taken up with nitric acid, and filtered. The filtrate was again evaporated, taken up, and filtered to recover some tungsten which still remained in solution. The tungsten trioxide was weighed as such: the bismuth was precipitated from the filtrate as the basic carbonate and was ignited to the oxide and weighed.

	Found.	Theory.
$Hg_2O + H_2O$.....	30.08%	30.36%
$WO_3 + Bi_2O_3$.....	69.93	69.64
Hg_2O.....	26.65	24.96
H_2O (by difference).....	3.71	5.40
WO_3.....	50.41	51.04
Bi_2O_3.....	17.36	18.60

The above results indicate that the ratio $3Hg_2O.2Bi_2O_3.11WO_3.15H_2O$ maintains for the mercurous salt. To be sure the mercury is much too high, and since the water was obtained by difference, it was, of course, too low. In the analysis the precipitate obtained was not pure mercurous chloride, but a mixture of mercurous chloride and some of the complex which had not completely transposed. On drying the mercurous chloride and this complex were weighed together. On ignition to expel the mercurous chloride some bismuth was also volatilized as the chloride, and any water which might have been retained with the complex would also be expelled. This all tends to make the mercury high. Considering this expected error, together with the good agreement of the $Hg_2O + H_2O$ and the $WO_3 + Bi_2O_3$, it is fair to conclude that the ratio is the same as that for the ammonium, potassium and strontium salts.

The body was well defined and thoroughly stable.

Having obtained the mercury salt the intention was to isolate the free acid and endeavor to obtain a non-ionizing solvent for it. If such a solvent could be obtained it would be possible to learn its molecular magnitude.

Hydrochloric acid was added in slight excess, and, after filtering from mercurous chloride, the solution was evaporated to dryness. The resulting body was not homogeneous. It was thought that the bismuthicotungstic acid might be more stable in neutral solution; accordingly the mercury salt was covered with water, and such an amount of hydrochloric acid was added as would leave a part of the salt undecomposed. After digesting several hours in the cold, with occasional shaking,

it was filtered. The water solution was evaporated, under reduced pressure, and at a low temperature. When the water was nearly all removed a greenish oily body separated. The last traces of water were allowed to evaporate at ordinary temperature.

After the water had evaporated large quantities of hydrogen chloride commenced to come off. The sample was placed in a desiccator, over sodium hydroxide, until the hydrogen chloride was completely removed. The body fell to a greenish yellow solid.

This behavior was remarkable. It was expected that the reaction would be

$$3Hg_2O.2Bi_2O_3.11WO_3 + 6HCl = 3H_2O.2Bi_2O_3.11WO_3 + 6HgCl.$$

When it was observed to contain hydrogen chloride it was first thought that the hydrogen chloride had added on in place of water of crystallization giving $3H_2O.2Bi_2O_3.11WO_3.xHCl$. Later behavior seemed to indicate that the hydrogen chloride had replaced the Hg_2O, and that it possessed some such composition as $6HCl.2Bi_2O_3.11WO_3$.

The compound, after losing its hydrogen chloride, was no longer soluble in water, or even acids. In an effort to find a solvent for it the following reagents were used: Alcohol, ether, acetone, pyridine, quinoline, nitro-benzine, benzene, toluene, aniline, acetic acid, carbon tetrachloride and carbon disulphide, none of which effected a solution. If the hydrogen chloride had merely added on, like water of crystallization, it would have been expected to redissolve in this acid.

The insolubility of this body rendered it useless as a material from which to determine the molecular magnitude.

It was noticed that the mercurous salt gave a colloidal suspension in acetone, and on adding hydrochloric acid, it entered into solution with the separation of mercurous chloride and some free mercury. It was hoped that the

free acid could be obtained from this solution, but on evaporating a dark green powder separated, which was not redissolved by acetone or acids.

On adding barium chloride to a solution of the ammonium salt a white viscous oil separated. This dried to a solid glass resembling the strontium salt.

CONCLUSIONS.

1. The mercurous salt of bismuthico-tungstic acid corresponding to ratios already obtained, was prepared, and was found to be a stable body.

2. Attempts to prepare the free bismuthico-tungstic acid were unsuccessful, and would lead to the conclusion that the acid $3H_2O.2Bi_2O_3.11WO_3$, like H_2CO_3 and many other acids, is so unstable as to exist only in the form of its salts.

3. When liberated from its mercury salt, with hydrochloric acid, the complex unites with the hydrochloric acid to form a compound which is only stable in solution.